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# QUARTERLY PROGRESS REPORT

OCTOBER 15, 1953

SOLID-STATE AND MOLECULAR THEORY GROUP  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY  
CAMBRIDGE, MASSACHUSETTS

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QUARTERLY PROGRESS REPORT NO. 10

SOLID-STATE AND MOLECULAR THEORY GROUP

Massachusetts Institute of Technology  
Cambridge, Massachusetts

O. N. R. Contract N5ori-07856

October 15, 1953

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Quarterly Progress Report No. 10

on

Project N5ori-07856

SURVEY

In the preceding Progress Report, there was considerable discussion of the theory of energy bands: we spoke of the use of a tight binding approximation as an interpolation method for handling the problem of energy bands at an arbitrary point in the Brillouin zone, and the orthogonalized plane wave method for getting accurate results at certain points of special symmetry in the zone. Our thinking along these lines has progressed a good deal in the intervening time. In the first place, in preparation for the course which I am proposing to give during the fall on the energy levels of impurities in crystals, I have been thinking further about the nature of Wannier functions, and about the relation of the simplified tight binding approximation to such problems. Dr. Koster has been assisting, and Dr. Schweinler has been making valuable suggestions in connection with these questions, and a short summary of some of our results is included in this Report, though they will be written up in more detail in the Technical Report No. 5, which will include the material to be given during this course. Some of the points which we are finding in this study begin to have a rather close relationship to the actual behavior of impurity levels in germanium and silicon, such as the possibility of two quite different sorts of impurity levels, hydrogen-like ones of the sort often discussed, and also much deeper-lying levels with the wave functions more concentrated around the impurity atoms. In this discussion of impurity levels, we had the benefit of a visit from Professor H. Jones of the Imperial College of Science and Technology, Dr. J. Friedel of the Ecole des Mines, and Professor C. Kittel of the University of California, during which the current state of such theory was discussed; much of the progress reported here, however, has been made since that visit during July.

The other aspect of the theory of energy bands in which we have made progress is an improvement in the orthogonalized plane wave method. Dr. Parmenter in the last Progress Report described a method which he has been applying to chromium; in thinking about that method, and about the method as proposed by Herring and applied to diamond by Herman, it occurred to me that there was a variation of the existing methods which might have some advantages over any of them. This consists in a scheme to satisfy Schrödinger's equation as accurately as possible within the atoms, where we assume spherical symmetry, and to fit such a solution onto plane waves outside the atoms, then making a linear combination of such augmented plane waves to get a final wave function. I had tried such a scheme, in 1937, but the method used then was not conveniently adapted to calculation, and it has had very little use. The new scheme, however, avoids the difficulties of the old one, and we hope that it may prove

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useful, and rapidly convergent. The mathematical development as I carried it through, involved some rather intractable infinite sums. However, when Mr. Saffren, who has newly joined the Group, looked into the mathematical formalism, he was able by a very ingenious application of Green's functions to show how these series could be summed, leading finally to a very simple and usable formalism. We hope that the method can shortly be applied to several crystals. We are fortunate in that Dr. D. J. Howarth, of the Imperial College, has just joined the Group for a visit of a year. He has been working with Jones on very accurate applications of the cellular method to sodium, copper, and other crystals. We are hoping that in collaboration with him we can work out a program of applying the new method to these same crystals, so as to compare the two rather different approaches. The results of accurate calculations of energy bands are so complicated that there is a very natural question as to how close the final results are to real solutions of the problem. Our confidence would be greatly improved by getting results by two methods which checked in their details. At the same time, such a comparison should show which method is easier to apply.

We come next to the many molecular calculations, principally involving configuration interaction, which are going on. In this connections, we include a report from Dr. R. McWeeny, of King's College, University of Durham, located at Newcastle-upon-Tyne, who has just joined the Group for a year's visit. Dr. McWeeny has been investigating problems of configuration interaction, and comparing the results with those obtained from simple wave functions constructed from molecular orbitals, and also with Heitler-London wave functions, constructed according to the standard Heitler-London method, but with the calculations carried out properly, involving all the terms usually omitted. His actual calculations have been made using orthogonalized orbitals, which we believe is the most practicable method for complicated systems. The interesting result which he finds is that the Heitler-London wave functions are rather close to the best wave functions derived from configuration interaction, much closer to them than are the molecular orbital wave functions. This is what we should suspect from the example of hydrogen, where it is certainly true. The importance of studies like that of McWeeny is that if we find that a wave function like the Heitler-London one really is rather accurate, we can then express this wave function as a combination of a number of configurations formed from orthogonalized orbitals (so as to put the calculations in a form which can readily be carried out), and it is likely to be a rather good first guess at the combination of configurations which will minimize the energy.

Any such guide to the correct configuration interaction will be of great value in more complicated problems, whereas we have seen in earlier reports a complete configuration interaction is too complicated to undertake. Such a use of the Heitler-London method is of course completely different from the misuse of the method which has so often been made, in which many integrals are neglected in the interest of simplification.

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Such approximations are not involved in the present method, which gets at the Heitler-London results through the use of configuration interaction methods with orthogonalized orbitals. These interesting results of McWeeny are included in this Progress Report, though they were obtained before he joined the Group, for two reasons: because they contribute so directly to the line of thought on configuration interaction which we have been following, and because he will continue to work along the same line, and make contributions to future progress reports based on the material presented here.

The calculation on antiferromagnetism which Dr. Pratt reports has a good deal of resemblance to that of McWeeny, in a way. In the previous Progress Report he had indicated the difficulty of getting a model of a molecule resembling  $(\text{MnOMn})^{++}$  which did not lead to ferromagnetism rather than antiferromagnetism, and we suspected that a configuration interaction was required to lead to the observed results. Since he did not seem to be able to choose the correct configurations to lead to the desired results, when expressed in terms of orthogonalized orbitals, I suggested that he set up the problem in terms of non-orthogonalized orbitals, following a Heitler-London model, using a simplified four-electron case which might lead to the antiferromagnetic sort of action, and carrying the configuration interaction through completely with the non-orthogonalized orbitals. This use of non-orthogonalized orbitals in a Heitler-London calculation, as I have pointed out before, very rapidly becomes entirely impossible as the number of electrons increases, but for four electrons it is still possible, though difficult. Fortunately this method seems to have worked; and now, by expanding the final wave function in terms of orthogonalized orbitals, Pratt has found which configurations are required to get the desired results, and which he had failed to include in his earlier work. It is interesting that this exact Heitler-London calculation can be compared with the simplified type of approximate use of the method which we feel is unreliable. In this case, even though the overlap integral is only of the order of 0.04, an error of about fifty percent is made by using the usual Dirac vector-model methods, neglecting overlap integrals and all exchange integrals except the two-center integrals. This certainly should put one on his guard against using that method for any work in which it is regarded as an accurate method of calculation.

Pratt's results are interesting physically, as well as pointing the way toward better methods of calculation. They show, more or less as in the discussion of the preceding Progress Report, that the physically important effect is a distortion of the oxygen atom (here replaced for simplification by a helium atom) by the two adjacent magnetic atoms. The detailed mechanism, however, is not that described in the preceding Progress Report, but instead is the process described as super-exchange, by Anderson and Van Vleck; we feel, in other words, that their mechanism is correct, even though we do not feel that the method used by them to compute it is reliable. There are two possible types of distortion, or polarization, of the oxygen atom, either

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of which could lead to a stabilization of the singlet state compared to the triplet. In either mechanism, the electrons of plus spin in the oxygen will be displaced toward one neighboring atom, those of minus spin toward the other, and this resulting deformation can lower the energy, being a form of polarization. The mechanism described in the preceding Progress Report was one in which the electron of plus spin from the oxygen wishes to be attracted toward the ion with plus spin, on account of Hund's rule. The opposite mechanism, the superexchange mechanism, is that in which it is attracted to the ion with minus spin, on account of an incipient covalent binding. One might well expect that the first would be the likely mechanism in case the magnetic ion had an only partially filled d shell, so that the oxygen electron attracted to it could enter this shell with the same spin without contradicting the exclusion principle; whereas the second mechanism would apply when all the orbitals of one spin in the d shell were filled, all those of the other spin empty, as in  $\text{MnO}$ , and as in the  $\text{He}^+$  model which Pratt used. In either case, Pratt's present contribution points the way to a quantitative method of handling the effect.

Another magnetic calculation, pointing out the complications of the problem and the dangers of trusting to over-simplified exchange integrals, is Kikuchi's calculation of the interaction of two p electrons, to see if they can have a ferromagnetic interaction, as in  $\text{O}_2$ . This very simple problem, as Kikuchi shows, leads to a four-by-four secular equation, and no one who has looked at his figure, illustrating the way in which the energy levels of singlet and triplet states vary with internuclear distance in this very simple problem, can doubt the extreme complexity of configuration interactions, and the dangers of oversimplifying them. It is very interesting that Kikuchi found a magnetic ground state over a range of internuclear distances, though the singlet lies lower at smaller internuclear distances, as it should from general grounds. But the behavior at large distances is so complicated that it is clear that no method based on simple exchange integrals, amounting to an extrapolation inward from infinite separation, could be reliable in such a case. Kikuchi's case is far enough from actual magnetic materials so that it can hardly be applied to an actual case, but it is very valuable to see how these problems work out in simple cases. Dr. Kikuchi has left the Group since the last Progress Report, to take a position at the University of Chicago, and his absence will be seriously felt.

Still another contribution to the study of configuration interaction is the result which Mr. Callen has obtained in his study of configuration interaction in hydrogen. Coulson a number of years ago showed that by getting a really good symmetric molecular orbital for the ground state of hydrogen, the molecular orbital energy was improved a good deal as compared to the calculations made using the LCAO MO's. Callen was interested in setting up an equally good antisymmetric molecular orbital, and then finding the result of a configuration interaction between just the two configurations



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in which both electrons are in the symmetric state, or both in the antisymmetric state. It is this type of configuration interaction using LCAO MO's which was discussed at length in Technical Report No. 3, and which includes the Heitler-London calculation as a special case, but which does not lead to very good numerical results. Callen has carried through this calculation, and his present result for energy lies among the better approximations to the hydrogen problem, aside of course from the James and Coolidge result, which is of quite different order of accuracy. He expects to be able to improve his energy somewhat by further varying his antisymmetric wave function.

The various other pieces of work under way in the Group are making progress, as described in the Report, though they have not reached a point of interesting results. There have been certain changes in the personnel of the Group, since the last Report, in addition to those already noted: Dr. Barrett has completed the term of his fellowship, and has left to take a position at the North Carolina State College, and Mr. Hunt has entered the Army.

## 1. WAVE FUNCTIONS FOR IMPURITY LEVELS

It is well known that the best method for handling the wave functions of perturbed periodic lattices is by means of the Wannier functions.<sup>(1)</sup> We can treat Schrödinger's equation in such a case by making a superposition of Wannier functions on different atoms, and in different energy bands. If  $a_n(\vec{r} - \vec{R}_i)$  is a Wannier function in the  $n^{\text{th}}$  band, located on the atom in the unit cell at vector position  $\vec{R}_i$ , then such a superposition is  $\sum (n, \vec{R}_i) U_n(\vec{R}_i) a_n(\vec{r} - \vec{R}_i)$ . Schrödinger's equation in the presence of a perturbative potential  $V$ , superposed on the periodic potential for which the original energy bands are calculated, reduces to a set of linear equations for the  $U$ 's, which can be written in the form

$$\sum (m, \vec{R}_j) H_{nm}(\vec{R}_i, \vec{R}_j) U_m(\vec{R}_j) = E U_n(\vec{R}_i). \quad (1.1)$$

The matrix components of the Hamiltonian,  $H_{nm}(\vec{R}_i, \vec{R}_j)$  are composed of the contributions from the periodic potential, which can be written  $\mathcal{E}_n(\vec{R}_i - \vec{R}_j) \delta_{nm}$ , and the matrix components  $V_{nm}(\vec{R}_i, \vec{R}_j)$  of the perturbation. We see that the periodic potential has no matrix components between Wannier functions in different bands, and that the matrix components between Wannier functions on different atoms but in the same band depend only on the displacement from one atom to the other.

The reason why the Wannier function method has appealed so much to the physical intuition is that the function  $U_n(\vec{R}_i)$  has itself many of the aspects of a solution of Schrödinger's equation. We may replace this set of coefficients, defined for discrete  $\vec{R}_i$ 's, by a continuous function  $U_n(\vec{r})$ . We may then approximate the secular equation for the  $U_n(\vec{R}_i)$ 's, which is a set of difference equations, by differential equations, and if the  $U$ 's vary slowly enough from atom to atom, these differential equations reduce to second order differential equations, which are equivalent to Schrödinger equations for a particle with an effective mass moving in the perturbative field. These approximations are not always very valid, however, and we have been looking into the straightforward problem of solving the difference equations, which is a much more valid procedure.

As an example of a case where the differential equation is definitely inapplicable, but where the difference equation method can be carried through, we may consider the problem of a perturbing atom in a three-dimensional crystal, in a case where we can get a good approximation by using the Wannier function of only one band. In particular, we have considered that  $V_{nm}(\vec{R}_i, \vec{R}_j)$  reduced to a single term, for  $n = m$  (since we consider only one band), and for  $\vec{R}_i = \vec{R}_j = 0$ . In other words, we assume that the perturbing potential is so concentrated that it is felt only on the central atom. This is not a bad approximation for the effect of an impurity atom in a metal, where the perturbative potential is known to be screened very strongly from even close neighbors. We have further simplified the problem to the case of a simple cubic lattice,

## (WAVE FUNCTIONS FOR IMPURITY LEVELS)

with matrix components  $\mathcal{G}_n(\vec{R}_i - \vec{R}_j)$  connected with only nearest neighbor interactions. In such a case the difference equation can be solved exactly, by an adaptation of a method used by McCrae and Whipple,<sup>(2)</sup> which was pointed out to us by Dr. Schweinler. We shall not reproduce the solution here; it is somewhat complicated, and will be given in detail in Technical Report No. 5. We can state the general results, however.

We can get a guide as to what to expect from the corresponding free electron problem, representing the differential equation which approximates the difference equation. This is the problem of a free electron with a deep spherical potential well near the origin, but otherwise in a constant potential. We know that this three-dimensional potential well problem, unlike the corresponding one-dimensional problem, does not have any solutions of the form of discrete energy levels unless the well exceeds certain critical dimensions. The reason is simple. The solutions of the three-dimensional problem inside the potential well is of the form  $\sin kr/r$ , and outside of the form  $e^{-\gamma r}/r$ . The functions  $\sin kr$  and  $e^{-\gamma r}$  must join continuously and with continuous slope at the boundary of the well. This is clearly impossible unless the function  $\sin kr$  has gone through at least a quarter wave length inside the well, so that it has risen above its maximum and is sloping down when it must join the decreasing exponential. If the well is just deep enough to join onto an exponential with negligible  $\gamma$ , the wave function outside falls off like  $1/r$ , and if it is deeper, the wave function  $e^{-\gamma r}/r$  falls off even faster than  $1/r$ .

Our study of the difference equation shows that here too there is a critical value of the perturbation of the potential on the central atom, which must be exceeded before a discrete level appears. Numerically, the perturbative term  $V_0$  must be equal to approximately a third of the band width before there is such a discrete state. By the time  $V_0$  becomes equal to something more than half the band width, the wave function of the discrete level is falling off so rapidly that almost the whole of the wave function is confined to the central atom. In any case, so long as there is a discrete state at all, the wave function falls off rapidly with  $r$  (as it falls off at least as fast as  $1/r$  in the case of the differential equation), and this is such a rapid variation with position that it is not legitimate in any case to replace the difference equation by a differential equation, for quantitative work. The differential equation is useful only as a general guide to the nature of the results.

Arguments of the type we have just been sketching, though worked out on the basis of the differential equation, have been used by Friedel<sup>(3)</sup> to discuss impurity levels in alloys; he makes much use of the fact that in some cases there are discrete levels, and in other cases not. Clearly this distinction can be important in the consideration of the effect of impurity atoms on energy bands. It appears in addition, however, that similar questions enter in the problem of impurity levels in semiconductors. The problem of perturbed levels in the presence of a Coulomb potential is

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quite different from that of the square well potential. We know that the differential equation has an infinite number of discrete solutions, rather than a finite number of zero as with the square well. Furthermore, the 1s wave function falls off like  $e^{-\gamma r}$ , rather than as  $e^{-\gamma r}/r$  as with the square well. For the problem of impurity levels in a dielectric, like germanium, with high dielectric constants, it is a familiar fact that the constant  $\gamma$  is so small that the wave function falls off only slightly from one atom to its neighbor. Thus in this case it is legitimate to replace the difference equation by the differential equation in the standard way, and that method should give good approximations.

There is one exception to this statement, however. In the Coulomb case, we assume that the significant matrix components of perturbative potential,  $V_{nm}(\vec{R}_i, \vec{R}_j)$ , come when  $n = m$ ,  $\vec{R}_i = \vec{R}_j$ , and we assume that the components  $V_{nn}(\vec{R}_i, \vec{R}_i)$  represent Coulomb energies, as modified by the dielectric constant, on atoms at a distance  $\vec{R}_i$  from the perturbing atom. On account of the large dielectric constant, these terms are small. On the other hand, the dielectric constant does not enter into the perturbative atom on the central atom itself. The term  $V_{nn}(0, 0)$  can be quite large. It is of course not infinite, as a Coulomb potential would be at the origin; for it represents the average of a perturbative potential of Coulomb form (without the dielectric correction) over the Wannier function on the central atom. Nevertheless it is a large term, which is not considered at all in the usual formulation of the hydrogen-like impurity levels in a semiconductor.

It appears likely that this term  $V_{nn}(0, 0)$  will act much like the corresponding term in the problem of a perturbation on a single atom, which we have already mentioned. That is, unless it exceeds a critical value, it is not likely to make much modification of the hydrogenic wave function and energy level, as usually considered. If it exceeds a critical value, however, it can modify the character of the wave functions completely, causing them to be concentrated much more closely around the perturbing atom, and can push the discrete energy level far away from the valence or conduction band. We must look in some cases, in other words, for energy levels midway between valence and conduction bands; this may well explain the origin of the deep trapping levels which are often observed in semiconductors. <sup>(4)</sup>

In the ordinary case of impurity levels, it is not legitimate to disregard the interaction of several energy bands, with their effect on the symmetry of the Wannier functions. It has already been pointed out <sup>(5)</sup> that the Wannier functions with overlapping bands have very complicated symmetry properties. In such a case, however, we believe that the most practicable approach is to use the simplified tight binding approximation <sup>(6)</sup> which has been discussed in the preceding Progress Report, and in Technical Report No. 4. As an example, let us take the diamond lattice, as in silicon or germanium. There it is possible to set up good approximations to the valence and conduc-

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tion bands by using eight types of atomic orbitals, the  $2s$ ,  $2p_x$ ,  $2p_y$ ,  $2p_z$  orbitals on each of the two atomic sites in the unit cell. We can now, to an equally good approximation, build up the wave functions of impurity levels by superposing the same types of atomic orbitals. That is, we set up a superposition  $\sum (n, \vec{R}_i) U_n(\vec{R}_i) \phi_n(\vec{r} - \vec{R}_i)$ , where the  $\phi$ 's are the atomic orbitals, to represent the wave function, where the summation is over these eight orbitals. The difference equations for determining the  $U$ 's are exactly of the form of Eq. (1), except that the matrix components for the periodic potential, instead of being  $\mathcal{O}_n(\vec{R}_i - \vec{R}_j) \delta_{nm}$ , are replaced by the matrix components of energy between the various orbitals set up in the tight-binding approximation in Ref. (6). If we choose these matrix components to be identical to those found in Ref. (6), chosen to give good agreement with the correct calculation of the energy bands at points in the Brillouin zone where they have been worked out by the orthogonalized plane wave method or other accurate approximation, then the wave functions of impurity levels set up in this way will be entirely consistent with the theory of the energy bands.

This procedure can be shown to be equivalent to the following much more complicated procedure: to solve for the energy bands (eight, in the case of the diamond lattice) by the tight-binding approximation, to compute Wannier functions from each one of the resulting (eight) energy bands, and to use these Wannier functions for determining the impurity wave functions, with use of interactions between all these Wannier functions. By using the atomic orbitals directly, we can see much more clearly the nature of the resulting impurity wave function. Each wave function will have a definite symmetry, transforming according to an irreducible representation of the point symmetry group of the crystal. We can then see at once that on each atom we must use combinations of the appropriate atomic orbitals so that the whole wave function will have the correct symmetry. This can often give us enough information so that we can predict in advance that many of the  $U_n(\vec{R}_i)$ 's must be zero, or have certain relations to each other. As an example of the sort of thing to expect, we should expect that an impurity level of s-like symmetry, constructed largely out of p atomic orbitals, would have the axes of these p orbitals pointing approximately radially inward or outward from the central atom. This is similar to the construction of a Wannier function of s-like symmetry, from p orbitals, discussed in Ref. 5.

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J. C. Slater and G. F. Koster

## 2. AN AUGMENTED PLANE WAVE METHOD FOR THE PERIODIC POTENTIAL PROBLEM

The cellular method, and the orthogonalized plane wave method, form two approximations to the solution of the periodic potential problem which are so well known that they need no comment.<sup>(1)</sup> Both of them take advantage of the fact that the potential is approximately spherically symmetric about each atom. In fact, we can get a good enough approximation to the periodic potential in a real crystal to serve as a starting point, by assuming that it is spherically symmetrical within atomic spheres, constant between the spheres; we may best, in such a case, take the spheres as large as possible, preferably touching. Then it is a natural hope that somehow we can build up good solutions of the composite Schrödinger problem, since we know how to solve this problem exactly within the atomic spheres where the potential is spherically symmetric, and also in a region of constant potential such as the region outside the atoms. One of the present writers<sup>(2)</sup> tried in 1937 to set up a solution in the form of a superposition of functions each of which was a plane wave between the spheres, joined continuously onto a solution of Schrödinger's equation within each of the spheres. Functions of this type had some resemblances to the orthogonalized plane waves introduced later by Herring for the same purpose, in that in each case it was recognized that the difficulty with using ordinary plane waves to solve Schrödinger's equation was that they formed such very poor approximations near the atoms. The method mentioned in Ref. (2) never had much application, because certain features made it very awkward and impracticable to use. The present note outlines a new scheme, with the same aim, which gives promise of being much more practical.

The whole problem is to take a single plane wave in the region between the spheres, and match this as well as possible to a solution of the spherical Schrödinger problem within each sphere. The matching cannot be perfect; it is well known from scattering theory that a plane wave outside a scattering atom can be matched to a solution inside only if we include scattered waves outside the atom. Our aim rather is to do the best matching job possible, and then take care of the scattering problem by superposing a number of such plane waves, which we may call augmented plane waves, since they contain an additional spherical contribution within each atom. Our augmented plane waves will be similar to Herring's orthogonalized plane waves, only we hope that by paying very close attention to satisfying Schrödinger's equation within the atoms we can make them better initial approximations to exact solutions, and consequently can make the process of combining a number of such augmented plane waves more rapidly convergent than by Herring's method. Herman and Callaway,<sup>(3)</sup> in their study of diamond and germanium, have shown that the process converges sufficiently fast to be usable. The reason why we prefer to handle the scattering problem by a superposition of plane waves, rather than of scattered wavelets, as in the problem of scattering by single atoms, is that using the plane waves we can immediately satisfy the periodicity conditions in the crystal, whereas if we superpose scattered wavelets,

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as Korringa<sup>(4)</sup> does, we have a major problem to satisfy these periodicity conditions.

The matching procedure which is now being proposed is the following. We start with a plane wave of definite propagation constant  $k$ , energy  $E_0$ , in the region outside the atoms, where the constant potential energy is set equal to zero, so that in atomic units  $E_0 = k^2$ . Around the boundary of an atom, we can expand this plane wave in a series of spherical harmonics of angle, and spherical Bessel functions of  $r$ , in the well known way. Inside the sphere, we now set up Schrödinger's equation for the assumed spherical potential, for each  $l$  value. We solve this equation using the energy as a parameter, taking the solutions regular at the origin, and find the logarithmic derivative of the function at the surface of the sphere, as a function of the energy. We pick out those particular energies, and eigenfunctions, for which the logarithmic derivative equals the logarithmic derivative of the corresponding spherical Bessel function encountered in the expansion of our particular plane wave. If we make any finite sum of such eigenfunctions, then, with coefficients so chosen that the function joins continuously onto the plane wave at the boundary, we shall find that the derivative of the function also joins smoothly; for the functions inside and outside have the same logarithmic derivative, or ratio of slope to function, at the joining surface. We can build up a function inside, then, joining smoothly onto the plane wave, in a very large number of ways, since we can give arbitrary coefficients to all of these eigenfunctions, subject only to the condition that the function be continuous at the surface of the sphere.

The next step in the procedure is to set up the expectation value of the energy, for the function which equals the plane wave outside the sphere, the arbitrary superposition of our eigenfunctions within the sphere, and to vary the arbitrary parameters to make the energy stationary. By so doing, we may hope to get the best approximate solution of Schrödinger's equation, consistent with equalling the plane wave outside the sphere, and joining smoothly onto it at the surface. Fortunately, this variation procedure can be carried through explicitly, without having to solve an unmanageable secular equation. We can set up an explicit formula for the resulting augmented plane waves and their energies. We find that, for a given  $k$  value, we have solutions of low energies, corresponding to the bound states of the atoms. The energies are almost exactly identical with those of the free atoms, and the wave functions are concentrated almost completely within the atoms, the amplitudes of the plane waves between the atoms being negligible. For higher energies, on the contrary, we have solutions which are much more like the ordinary orthogonalized plane waves: they are of comparable magnitudes inside and outside the atoms, joining smoothly over the surface of the atom. These functions have some very useful properties. Functions of the same  $k$  value are automatically orthogonal (so that we have achieved the orthogonalization which Herring uses) and have no non-diagonal matrix components of energy



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between them, since they are derived from a variation method. We have non-vanishing non-diagonal matrix components of energy between augmented waves of different  $k$  values, however, and these components are easy to compute, and are the quantities required in setting up the linear superposition of augmented plane waves which is to be used as an approximation to the true wave function.

The method in this form was worked out by one of us (JCS), and is appearing in a forthcoming number of the Physical Review. It has the disadvantage that, though the formulation is simple and explicit, still it contains a number of infinite sums, in the form of sums over the eigenfunctions of the problem of solving Schrödinger's equation within the sphere, subject to the boundary condition of having a prescribed logarithmic derivative at the surface of the spheres. The other of the present writers (MMS), examining this formulation, noticed that these infinite sums represented the expansions of certain Green's functions, in series of the eigenfunctions so set up, and it occurred to him that one could write these Green's functions directly, thus in effect finding explicit expressions for these infinite sums. This has now been done, with a resulting great simplification of the formalism of the method, but at the same time with an alternative physical description, which shows us exactly the nature of the final wave functions and energy levels. We shall first state this alternative description, then give the resulting mathematical formulation.

This alternative physical description proves to be the following. We start as before with the plane wave outside the spheres. We now set up a solution of Schrödinger's equation within the sphere for an arbitrary energy  $E$ , soon to be determined. For any such energy  $E$ , we can at once set up a solution which is continuous with the plane wave, but the derivative will not in general be continuous. We can then compute the expectation value of the energy, for the wave composed of this solution of Schrödinger's equation inside the sphere, and the plane wave outside. This expectation value will have as two of its terms  $E_0$  times the integral of the square of the plane wave over the region outside the spheres, and  $E$  times the integral of the square of the wave function over the inside of the spheres. There is a third contribution, however, coming from the discontinuity of slope of the wave function on the surface of the sphere. This discontinuity in slope can be considered a limiting form of an infinite second derivative, which integrates to a finite contribution to the kinetic energy, when we integrate over a thin spherical shell at the surface of the atom. We now take this resulting expectation value of the energy, and make the requirement that it be stationary when we vary the energy  $E$  inside the spheres. When we do this, we find that the resulting equation can be satisfied in a simple fashion: the expectation value of the energy is set equal  $E$ , the energy for which we are solving Schrödinger's equation inside the sphere. In other words, we have achieved an exact solution of Schrödinger's equation for the energy  $E$  inside the spheres, and the discrepancy in energy resulting

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from the fact that the energy of the plane wave part of the wave function outside the spheres is  $E_0$  is compensated by an equal and opposite contribution from the surface integral.

The mathematical formulation of this statement of the method is very simple, and we shall give its essentials in a moment. The interesting fact, however, is that we can take the solutions of Schrödinger's equation for the energy  $E$ , as encountered in this method, and expand them in terms of the eigenfunctions used in the earlier method, where we set up eigenfunctions of the problem with a prescribed logarithmic derivative at the surface of the sphere. When we do this, we can easily show that this method is identical with the other one, the infinite sums encountered in the earlier formulation becoming formally identical with much simpler functions found in the new method. We see, in other words, that the variation problem, set up in the older version of the method, coupled with the expansion of the solution of Schrödinger's equation inside the sphere in terms of an infinite sum of eigenfunctions all having a prescribed value of logarithmic derivative at the surface, so as to produce continuity of slope as well as function with the plane wave, has automatically built up a solution inside the sphere which does not have continuity of slope with the plane wave. It does, however, have the property we have just mentioned, that it satisfies Schrödinger's equation exactly inside the spheres, and uses the discontinuity of slope to compensate for the fact that it does not satisfy it exactly outside the spheres. It still appears that these functions should form a very good starting point for a secular problem involving a number of such augmented plane waves.

The mathematical formulation is now very simple. Let an atomic sphere be located at the origin, with a radius  $R$ . Let  $u_l(E; r)$  be the radial part of a solution of Schrödinger's equation for the interior of the sphere, with aximuthal quantum number  $l$ , and energy  $E$ , and regular at the origin. Then, using the familiar expansion of the plane wave, the solution of Schrödinger's equation for energy  $E$  inside the sphere, continuous with the plane wave of unit magnitude outside, can be written

$$\sum (l)(2l+1) i^l j_l(kR) P_l(\cos \theta) \frac{u_l(E; r)}{u_l(E; r)}; \quad (2.1)$$

when  $r = R$ , this at once reduces to the expansion of the plane wave at radius  $R$ . We can then show easily that the contribution of the surface discontinuity to the expectation value of the energy is

$$4\pi R^2 \sum (l)(2l+1) j_l^2(kR) \left[ \frac{d \ln u_l(E; r)}{dr} - \frac{d \ln j_l(kr)}{dr} \right]_{r=R} \quad (2.2)$$

## (AUGMENTED PLANE WAVE METHOD)

The last term in the square bracket can be eliminated, if we choose, by using the relation

$$\sum (l)(2l+1) j_l(z) \frac{dj_l(z)}{dz} = 0,$$

which can be proved from the properties of spherical Bessel functions. The contribution of the plane wave to the discrepancy between the expectation value of the energy and  $E_0$  is  $\Omega(E_0 - E)$ , where  $\Omega$  is the volume of space outside the sphere. Since our condition on  $E$  is that this discrepancy, plus the contribution of the surface discontinuity to the energy, must add to zero, our condition for the energy is found by setting the expression (2) equal to  $\Omega(E - E_0)$ . We are left, then, with

$$\Omega(E - E_0) = 4\pi R^2 \sum (l)(2l+1) j_l^2(kR) \left. \frac{d \ln u_l(E;r)}{dr} \right|_{r=R} \quad (2.3)$$

as the condition for the energy. We can solve this by plotting the right side as a function of  $E$ , and finding the intersection of this curve with the straight line represented by the left side. The details of the resulting conclusions regarding the energy levels are given in the next contribution to this Progress Report.

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J. C. Slater and M. M. Saffren

### 3. ENERGY RELATIONS IN THE AUGMENTED PLANE WAVE METHOD

In order to discuss the solutions of the energy (Eq. 2.3 of this Report), we plot both the left-hand and right-hand members of the energy expression as functions of the energy, the intersections of these curves giving us solutions. The left-hand member is simply a straight line with slope  $\Omega$  which intersects the energy axis at  $E = E_0$ . The right-hand member is a superposition of the curves  $d \ln u_l(E; r)/dr|_{r=R}$  taken with the weight  $4\pi R^2(2l+1) j_l^2(kR)$ . Any such curve will have infinities for those values of energy which cause  $u_l(E; R)$  to equal zero. Since the slope of such a curve must be everywhere negative, as we can show, the curve will have a strong resemblance to a cotangent curve. This behavior is consistent with what we should expect if we approximated our wave functions  $u_l$  by the WKB method. For energies which are very negative the solutions to the Schrödinger equation are essentially a combination of the exponentials

$$\frac{e^{-\sqrt{|E|}r}}{r} \text{ and } \frac{e^{+\sqrt{|E|}r}}{r}.$$

Thus for  $r = R$  the wave function is practically the increasing exponential, and our curve is essentially the parabola  $\sqrt{|E|} - 1/R$ . As we come to the first bound state the increasing exponential comes in with a smaller and smaller contribution until it disappears completely, and then, soon after, the wave function vanishes. For very negative energies the bound state occurs at the intersection of the curve and the parabola  $\sqrt{|E|} - 1/R$ . This behavior repeats for the other very tightly bound states. As the energy increases further the decreasing exponential becomes increasingly important at  $r = R$ , so that between two infinities in the curve, the slope changes more gradually. As the energy increases still further, the many oscillations in the wave functions reach the point  $r = R$ , and the curve takes on more and more a cotangent behavior. In the region about zero energy the shape of the curves will depend strongly on the shape of the potential. In the region of large positive energy the wave function will essentially be a spherical Bessel function with a small admixture of spherical Neumann function, and the curve is sensibly a cotangent curve. This description is summarized in Fig. 3-1. As the angular momentum increases, the wave function must go out further and further in distance before it builds up. It also dies out more gradually and so, for a bound state, can tie on only to a decreasing exponential which dies out more gradually. Collecting the consequences of raising the angular momentum we can say: the first bound state occurs at higher energy the higher the angular momentum; the effect of the decreasing exponential is felt more and more even in lower energies; the oscillations in the wave function are felt at  $r = R$  earlier in energy; and the shape of the curve about zero energy depends less and less upon the shape of the potential in the inner regions. For very high angular momenta there are

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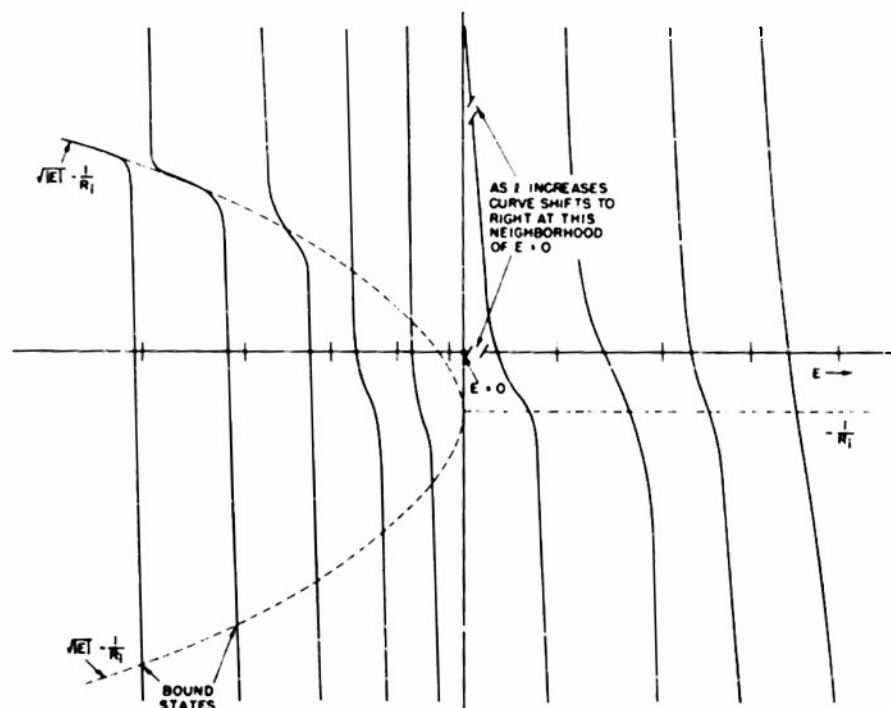


Fig. 3-1

Plot of  $\frac{u'_{il}(E; R_i)}{u_{il}(E; R_i)}$  as a function of  $E$  for small  $l$

no bound states and for negative energies the curve is essentially equal to the angular momentum quantum number,  $l$ , until it drops gradually to zero and then down to minus infinity, becoming for all higher energies a cotangent curve. This occurs because for high energies the wave function is essentially a spherical Bessel function whose behavior is just as stated.

We can now picture the curve of energy of the wave function as a function of the energy of the plane wave. This curve is traced out if we plot the energy values at which the straight line  $\Omega(E - E_0)$  cuts the cotangent-like curve  $4\pi R^2 \sum (l)(2l+1) j_l^2(kR) \frac{d \ln u_l(E; r)}{dr} \Big|_{r=R}$  as the energy of the plane wave increases indefinitely. If we call the continuous portion of the curve between two singularities (two adjacent singularities will in general belong to wave functions of different angular momenta) a "branch" of the curve, then to each such branch of the cotangent-like curve there corresponds a branch of the  $E$  vs.  $E_0$  curve. Each of these branches falls between lines of constant energy  $E$ , and these lines occur at all those energies for which any one of the wave functions  $u_l(E; R)$  vanishes. As the plane wave increases in energy the cotangent-like curve changes shape but each branch remains confined between the two asymptotes which bound it and these do not change position as the plane wave increases in energy.

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At the same time the straight line  $\Omega(E - E_0)$  moves down the energy axis with fixed slope cutting the axis at  $E = E_0$ . Let us picture what happens in a typical branch centered about  $E = E'$ . When  $E_0$  is very much less than  $E'$  the straight line will intersect the branch very close to its left-hand asymptote because the straight line will have achieved quite a large value before it intersects this branch, and only those portions of the branch near the asymptote can reach that high. As  $E_0$  approaches  $E'$ , the straight line will cut the branch at points which are closer to the right-hand asymptote. However, suppose  $E_0$  nears a value which causes  $j_l(kR)$  to vanish and  $l$  is the angular momentum quantum number equal to the index of the wave function  $u_l$  which generates the left asymptote. Then as the plane wave energy nears that point, the contribution of  $d \ln u_l(E; r) dr \Big|_{r=R}$  to the cotangent-like curve nears zero except at the points where it has its singularities. At these points the branches to either side of the singularity will be slowly changing except very close to the asymptote where they tend to flatten out against it and then sharply achieve singular value. The closer the plane wave energy to the point which causes this behavior the more pronounced the behavior becomes. If this point at which  $u_l(E; R)$  vanishes is sufficiently distant from the branch, the intersection of the branch with the straight line nears the energy of the asymptote as the plane wave energy increases. This causes the  $E$  vs.  $E_0$  curve to dip down to its asymptote and, as  $E_0$  goes beyond this point the curve, rises again to resume its regular behavior. The result is that the  $E$  vs.  $E_0$  curve is tangent to its lower asymptote at such a point. Now let us suppose that the plane wave energy has passed such a point and is nearing  $E'$ , the location of the branch. Then the intersection moves across the branch until, when  $E_0$  is very much greater than  $E'$ , the intersection is made with values of energy near the right-hand asymptote. The behavior of the energy curve when  $E_0$  yields a root of a spherical Bessel function with  $E_0 \gg E'$  the same as that in the previous case mentioned except that now the energy curve dips up to meet the upper asymptote of the energy branch.

Thus if we draw lines of constant plane wave energy at all of those energies for which any one of spherical Bessel functions vanish, then when these lines intersect the asymptotic lines, the energy curve will be tangent to the asymptotic line at this intersection only if both these lines correspond to the same angular momentum and also if this intersection is sufficiently distant from the region in which  $E = E_c$ . Every spherical Bessel function except that of order one vanishes at  $E_0 = 0$ . Thus, every energy curve will start off at  $E_0 = 0$  touching its lower asymptote if that asymptote corresponds to any angular momentum other than zero and also if that asymptote is sufficiently distant from zero energy. There is a ramification of this peculiar event in the properties of the wave function which shall not be examined here. We now discuss the shape of the curve for negative energies.

It is clear that the branches with very negative energies will intersect the

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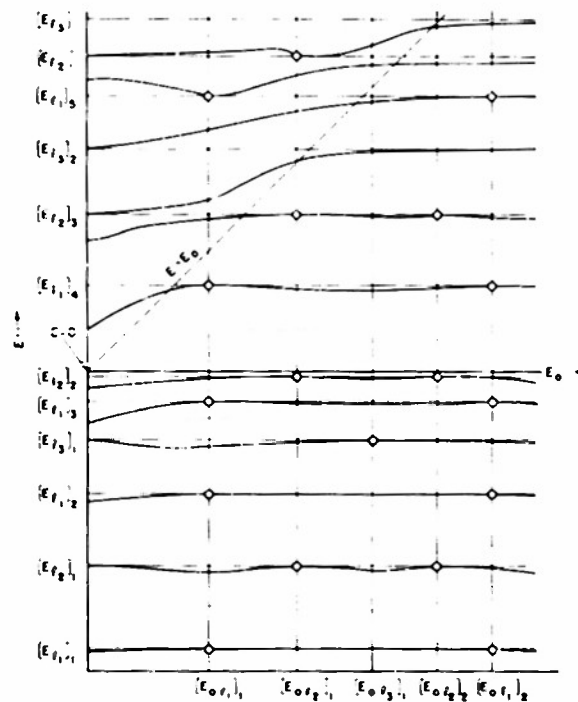


Fig. 3-2

Energy of an augmented plane wave as a function of the energy of its plane wave portions. (Circled points denote points of tangency.)

straight line very near the right-hand asymptote for all plane wave energies (we discount for the moment the peculiar behavior mentioned above). For the less tightly bound states, however, there remains the possibility that if the branch is sufficiently depressed the energy curve can start off near the left asymptote and then rise to the right-hand asymptote very much as the positive energy branches do. At least, there can be a remnant of such behavior for these branches. We have already mentioned that the asymptotes for very negative energies are very close to the energies of the strongly bound states so we see that the bound state energies are essentially independent of  $E_0$ . It is also clear that the peculiar behavior associated with the vanishing of a spherical Bessel function will occur also for negative energies, except perhaps for those states near zero energy. The energy curve is shown in Fig. 3-2. The shape of this curve along the line  $E = E_0$  is reminiscent enough of energy bands and the true periodic problem to suggest that these portions of the energy curves are rough approximations to a band structure. It also suggests which of the augmented plane waves to choose when we wish initial functions for our periodic problem when we attempt solutions for the higher bands.

Since the straight line has the slope  $\Omega$ , it should be clear that the effect of

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increasing  $\Omega$  is to make the onset of the rise of the energy curve near  $E = E_0$  more sudden and to make the curve everywhere else practically identical with the asymptotic values. The effect for negative energies is a tendency to remove the structure from the energy curves around the region  $k = 0$ . However, it should be noted that the effects of making  $\Omega$  larger is slightly compensated in the case of negative energy by the decrease in  $R$ , the compensation arising from a depression of the cotangent-like curve in that energy region. There is still a third factor. The curve will take on positive energy behavior much later in negative energy. This effect also tends to compensate the increase in  $\Omega$ .

M. M. Saffren



#### 4. ENERGY BANDS IN CHROMIUM

The calculation of matrix elements for the augmented orthogonalized plane wave method is in progress. In order to calculate kinetic energy integrals and Fourier transforms of the atomic orbitals it is most convenient to express these atomic orbitals as simple analytic functions. In conjunction with A. J. Freeman, the ion-core atomic orbitals of chromium have been so expressed. At present this process is being carried out for the modified 3d orbital discussed in the last Progress Report.

R. H. Parmenter

## 5. A REVISED VALENCE BOND THEORY

Recent work<sup>(1)</sup> has shown that it is possible to carry through completely non-empirical calculations on simple molecules using a revised form of the valence bond (VB) theory; since this method is to be developed during the coming year it seems desirable to report briefly on what has already been accomplished and on plans for further work.

The conventional VB theory proceeds in the following way: electrons are allotted to the AO's  $a$ ,  $b$ ,  $c$ , -- in some way (usually there is just one electron in each orbital but in so-called "polar" functions doubly filled (- ve) and empty (+ ve) orbitals occur -- these are not, however, invoked in the usual approximation). Spin factors are then added to give a product function such as  $U = a(1) \alpha(1) b(2) \beta(2) c(3) \beta(3) \dots$  and an antisymmetrized product (AP) is constructed;  $\phi = \mathcal{A}U = |(aa)(b\beta) \dots|$  say. A large number of eligible  $\phi$ 's arises because there are many possible spin allocations; but these  $\phi$ 's may be grouped into combinations which are spin eigenfunctions (SE's) and, in constructing an approximate wave function, only those SE's with similar eigenvalues of the operators  $S^2$  and  $S_z$  can be mixed. It is usual to consider a singlet ground state and to employ SE's formed by coupling the spins in pairs -- these are the "structures" (we shall denote them by  $\psi$ 's) of VB theory.<sup>(2)</sup> Finally, approximate wave functions ( $\Psi$ 's) are constructed in the basis of  $\psi$ 's. By analogy with the Heitler-London calculation on  $H_2$ , a single structure might be expected to describe a system of "bonds", each bond involving orbitals with paired spins: but, as Slater has pointed out for the  $H_2$  case,<sup>(3)</sup> spin-pairing alone is no criterion for bonding, for a change in character of the AO's may lead to a  $\psi$  predicting strong repulsion. A VB energy calculation generally becomes feasible only with the neglect of overlap between different AO's; in other words, conventional energy calculations, employing a basis of VB structures, can only be rigorously validated by a preliminary orthogonalization of all orbitals; and our experience with the hydrogen molecule shows just how crucial a step this may be.

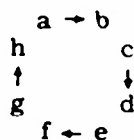
In the revised theory we do indeed start from a set of localized but orthogonal orbitals  $\bar{a}$ ,  $\bar{b}$ ,  $\bar{c}$ , -- (we shall call these  $\bar{AO}$ 's), constructed from the basic AO's  $a$ ,  $b$ ,  $c$ , -- by the method of Löwdin.<sup>(4)</sup> It is then possible to preserve the essential formalism of the VB approach, while completely avoiding the approximations of the usual treatment. But the characteristic features of the VB method are found to have completely disappeared: the " $\bar{VB}$ " structures of the new theory (i. e., structures defined over  $\bar{AO}$ 's rather than AO's) do not describe systems of chemical bonds in any sense whatever; in fact, the conclusions reached by Slater in the case of  $H_2$  are found to be quite general -- no single "covalent"  $\bar{VB}$  structure can describe chemical binding, predicting instead strong repulsion at all internuclear distances. Moreover, the situation cannot be restored by the introduction of any number of alternative non-polar  $\bar{VB}$  structures: in order to describe a bond involving orbitals  $\bar{a}$  and  $\bar{b}$  it is absolutely essential to admit polar  $\bar{VB}$  structures so that the final wave function will contain, with substan-

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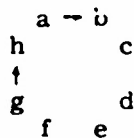
tial weight, pairs of structures which differ by a "shift of charge" between the orbitals  $\bar{a}$  and  $\bar{b}$ . The bond a-b therefore arises as an inter-configurational effect from the pairs of structures associated pictorially with a charge "hop" between atoms a and b. This conclusion is readily interpreted in terms of the molecular charge density function. The basic AO's have been replaced by distorted AO's ( $\bar{AO}$ 's) and, in the absence of polar structures,  $\Psi$  can only lead to a density of the form  $P = \bar{a}^2 + \bar{b}^2 + \bar{c}^2 + \dots$ ; but the  $\bar{AO}$ 's are clearly so distorted as to give a particularly low charge density in the bond regions. The high internuclear charge density, with which binding is associated, is introduced by the cross terms in  $\Psi^2$  which come from structures related by a charge hop.

Calculations by the "VB" method, obviously require the use of both non-polar and polar (possibly including multiply-polar) VB structures and consequently the calculation of matrix elements for all types of pair. This problem has been solved by an extension of the cycle method of Eyring and Kimball; <sup>(5)</sup> the results will be presented here without proof.

Any singlet structure is a combination of  $\phi$ 's which shows antisymmetry in the spin factors of various orbital-pairs; in the Rumer notation such a structure might be



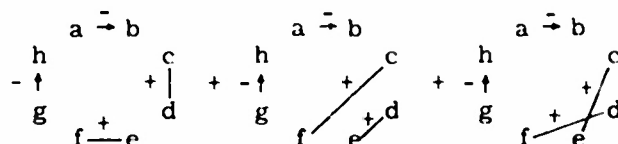
where the pairs are shown linked and the arrow indicates the order of the spin factors ( $\alpha \rightarrow \beta$ ) in the leading (or "parent")  $\phi$  of the SE combination. \* Triplet, quintuplet, -- structures arise when antisymmetry exists for one, two, -- less than the full number of possible pairs, the combination being symmetric in the spins of all the unpaired orbitals. But (at least for not too high multiplicity) such an SE is expressible in terms of a small number of completely paired structures in which some pairs are now associated with spin symmetry. Thus, the quintuplet SE



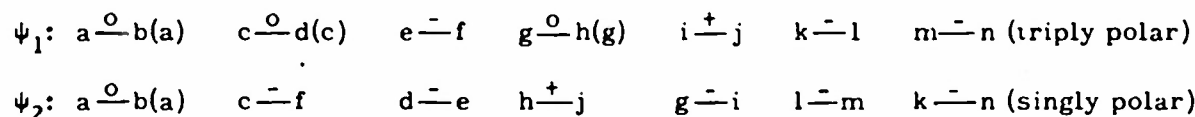
\* -----  
Reversal of an arrow simply changes the sign of a  $\psi$ ; directions are therefore unimportant except in determining the sign of a matrix element.

# (A REVISED VALENCE BOND THEORY)

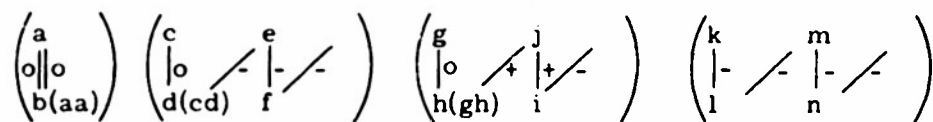
is equivalent to the combination



where we now distinguish the two symmetry types by + and -. New configurations may be introduced by substituting a new orbital for one of those in the standard set a, b, c, -- (indicated, for example, by f(k)): in particular, polar structures occur when the orbitals at the ends of a (-) link are identified. Thus a—b(a) indicates that orbital b has been replaced throughout by a - giving, when the orbitals are differently localized, a—b<sup>+</sup>; but the possible spin interchange between linked orbitals becomes redundant in this case and the link should be distinguished as a "dummy" or (o) link. The matrix element for any pair of spin-paired structures and the full Hamiltonian H may now be written down by inspection of a cycle diagram (set up by the method of Eyring and Kimball, disregarding new link-types and orbital substitutions), all links being inserted so as to give a continuous non-crossing chain in each cycle. Thus, for two typical triplet state structures with the following pairing schemes



the cycle diagram is



where, for instance, d(cd) means that d is substituted by c in  $\psi_1$  but left unchanged in  $\psi_2$ . It will be noticed that vertical links refer to  $\psi_1$  and diagonal to  $\psi_2$ . The required matrix element is then

$$(\psi_1 | H | \psi_2) = 2^{n-n_f} \left[ Q' - \sum \lambda_{pq} K'_{pq} - \sum \mu_{pq} K'_{pq} \right]$$

where  $Q = (abcd \text{ -- } |H| \text{ -- } abcd \text{ --})$ ,  $K_{pq} = (pq|g|qp)$  ( $g = 1/r_{12}$ ),  $n$  is the number of cycles,  $n_f$  being the number containing (0) links only, and

# (A REVISED VALENCE BOND THEORY)

| <u>p, q in different cycles</u> | <u>p, q in the same cycle</u>   |
|---------------------------------|---|
| $\lambda_{pq} = 1/2$            | $\lambda_{pq} = 1$ p, q same side.  |
|                                 | $\lambda_{pq} = 0$ p, q different sides.  |
| $\mu_{pq} = 0$                  | $\mu_{pq} = \pm 1$ according as the number of (-) links in each path between p and q is even or odd -- (0) links regarded as equivalent to (-). |
|                                 | $\mu_{pq} = 0$ p, q joined by a (0) link or by a chain of (0) links only.   |

There is no contribution if any cycle contains an odd number of (+) links. The primes on the Q's and the K's indicate that the standard set of orbitals a, b, c, -- may be modified, in either  $\psi_1$  or  $\psi_2$  or in both, by orbital substitutions: the sums extend over distinct pairs, p, q and  $K'_{pq}$  vanishes unless the pair p, q includes the one or two orbitals in which  $\psi_1$  and  $\psi_2$  may differ. Application of the rule is very simple; in the present case we see immediately  $(\psi_1 | H | \psi_2) = 2^3 [Q_{bdh}(aa, cd, gh) - \frac{1}{2} K_{dg}(cd, gh)]$  where  $Q_{bdh}(aa, cd, gh) = (a^a c^c d^d g^g h^h | H | a^a b^b c^c d^d e^e f^f g^g h^h) --$  and  $K_{dg}(cd, gh) = (d^d g^g | g^g l^l | g^g d^d)$ , the raised letters indicating the substitutions to be made. These quantities are always immediately expressible in terms of one- and two-particle integrals; in the present case Q' reduces simply to  $(cglldh) --$  a generalized Coulombic integral which might, in the present notation, have been called  $J_{dh}(cd, gh)$ .

The method outlined is quite general: but in dealing with the VB structures, where the orbitals which we have labelled a, b, c, -- are in fact the  $\bar{AO}$ 's  $\bar{a}$ ,  $\bar{b}$ ,  $\bar{c}$ , -- certain features of the subsequent energy calculations are particularly noteworthy. They are

(1) The only large integrals, which determine the essential structure of the final secular equations, are of the types  $\bar{\alpha}_a = (a|h|a)$ ,  $\bar{\beta}_{ab} = (a|h|b)^*$  and  $\bar{\gamma}_{ab} = (ab|g|ab)$ ,  $\bar{\alpha}$  and  $\bar{\beta}$  being the two integrals which would dominate a molecular orbital treatment. All generalized Coulombic integrals (such as  $J_{dh}(cd, gh)$ , above) and all exchange and generalized exchange integrals are very much smaller, when defined over  $\bar{AO}$ 's, than in conventional treatments.

(2) Intra-configurational matrix elements contain only  $\bar{\alpha}$ 's and J's (plus insignificant exchange terms); they arise from groups of structures which describe non-bonded atoms interacting as independent units --  $Q' = (abbd - |H|abbd --)$ , for instance, represents the energy of a system with one electron on a, two on b, none on c and one on d, including mutual repulsions.

\* h is the "effective" Hamiltonian for one electron in the field of nuclei and closed shells.

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(3) Inter-configurational elements contain only  $\bar{\beta}$ 's (plus insignificant exchange terms),  $\bar{\beta}_{ab}$  arising from pairs of structures differing by a shift of charge between the atoms about which  $\bar{a}$  and  $\bar{b}$  are localized, and being simply the "resonance" or "hopping" integral of MO theory. It is the presence of these elements alone which allows us to account for chemical binding, within the VB scheme.

Detailed numerical calculations are now in progress on the  $\pi$  electron systems of three organic molecules -- ethylene, cyclo-butadiene and benzene. \* The first case is trivial; but is useful because it admits a comparison between non-empirical estimates of  $\bar{a}$  and  $\bar{\beta}$  and the best empirical values (from ionization potential and spectral data). The second case is important because it makes possible a comparison of the VB procedure with the complete MO treatment given by Craig, <sup>(6)</sup> who used for the singlet states, for instance, a basis of twenty MO configurations (in our approach we employ twenty VB structures). In the third case it will be possible to make a similar comparison with the (much heavier) benzene molecule calculations of Parr, Craig and Ross, <sup>(7)</sup> who employ limited configuration interaction (using, for instance, the 45 lowest singlet configurations): it is felt that their results may be more easily reached and extended by using the VB approach. In all these cases it is possible to rigorously compare, for the first time, the rapidity of convergence of two approximation techniques which proceed from completely different starting points.

Results of some importance have already emerged. In both ethylene and cyclobutadiene it is instructive to set up suitable approximate wave functions in terms of the conventional VB structures (such functions being here determined completely by symmetry): these cannot be properly handled in the usual treatment -- but the Heitler-London calculation suggests that they are plausible wave functions; and we may now expand them in terms of VB structures and carry out a rigorous energy calculation. It turns out that the functions constructed in this way resemble quite closely the best approximations which can be obtained in the given basis; they are considerably superior to corresponding one-configuration MO functions. The expanded VB functions somewhat underestimate the weights of the polar VB structures, almost completely omitting the small multiply-polar contributions which feature in the best approximations. On the other hand, the (one-configuration) MO method grossly overweights all the polar structures and strong configuration interaction is necessary to correct this obvious defect. It seems likely that these results may be general and that the conventional VB structures may be of great value in indicating those groupings of VB structures which are most useful as "units" from which good approximate wave functions may be rapidly constructed; a preliminary energy calculation could then be

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\*The "separation" of  $\pi$  electrons from those of the closed shells is a valid first approximation provided the effective Hamiltonian  $h$  is properly defined.

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made in the "VB basis" (using, of course, the VB methods we have developed) and subsequent refinement, where practicable, could be made in the full basis of VB structures. This final step would usually be precluded by the large number of structures to be considered; for this reason the calculations on benzene, which should give more conclusive evidence of the efficacy of the simpler procedure, are of special interest.

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R. McWeeny

## 6. ANTIFERROMAGNETISM

In the preceding Progress Report an investigation of the  $\text{Mn}^{++}-\text{O}^{=}-\text{Mn}^{++}$  system was presented. As stated before, the object of this work was to find out how the spins of two magnetic ions, whose wave functions do not overlap, are coupled when they are separated by an intervening non-magnetic ion. Within the framework of the approximation made there, it was found that the Mn ions coupled ferromagnetically, i.e., the net spins of these ions were found to be parallel in the lowest state of the system.

In order to examine this problem of spin coupling in greater detail a much simpler model was investigated. This simplified system is shown in Fig. 6-1. The one-

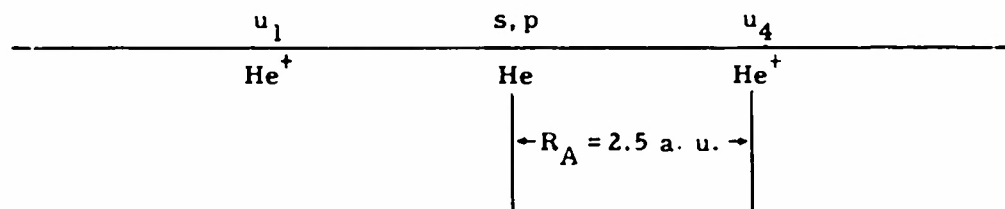


Fig. 6-1

electron orbitals used were gaussians localized about the various centers. Let  $u_1$  denote an s-like gaussian about the left-hand  $\text{He}^+$  and  $u_4$  an s-like gaussian about the right-hand  $\text{He}^+$ . Let  $s$  and  $p$  denote an s-like and p-like gaussian respectively about the central He. Two types of interactions were considered and their magnitudes compared. The first type was the spin coupling of the electrons on the two end  $\text{He}^+$  ions brought about by configurations in which the electrons on the central He were excited into higher states of that atom but were not transferred to one of the end  $\text{He}^+$  ions. These configurations are listed in Table 6-1.

Table 6-1

| $u_1$ | $s$ | $p$ | $u_4$ |             |
|-------|-----|-----|-------|-------------|
| 1     | 2   | 0   | 1     | $\psi_{ss}$ |
| 1     | 1   | 1   | 1     | $\psi_{sp}$ |
| 1     | 0   | 2   | 1     | $\psi_{pp}$ |

The second type of interaction investigated was the spin coupling of the two end  $\text{He}^+$  ions brought about by the superexchange configurations,<sup>(1)</sup> in which one electron is taken from the central He and placed on one of the end  $\text{He}^+$  ions. These configurations are listed in Table 6-2 where only  $s$  orbitals were considered in this case.

It was felt that by using non-orthogonal orbitals for this simple model some light might be thrown on the question of whether or not the use of orthogonal one-electron orbitals and a rather limited configuration interaction for the  $\text{Mn}^{++}-\text{O}^{=}-\text{Mn}^{++}$



Table 6-2

| $u_1$ | s | $u_4$ |          |
|-------|---|-------|----------|
| 1     | 2 | 1     | $\psi_0$ |
| 2     | 1 | 1     | $\psi_1$ |
| 1     | 1 | 2     |          |

problem was responsible for the result found there. Also the results for this simple system can be re-expressed in terms of orthogonal orbitals showing what configurations of orthogonal orbitals would give an equivalent result.

The overlap matrix,  $m_{ij} = \int u_i^* u_j dv$  is given in Table 6-3. The orbitals  $u_1$  and  $u_4$  were assumed not to overlap, i. e.,  $u_1(x) u_4(x) = 0$  for all  $x$ . The non-orthogonality was carried through completely no overlap integrals or three-center integrals being neglected.

Table 6-3

|       | $u_1$            | s                | p                | $u_4$            |
|-------|------------------|------------------|------------------|------------------|
| $u_1$ | 1                | $\delta_{u_1 s}$ | $\delta_{u_1 p}$ | 0                |
| s     | $\delta_{u_1 s}$ | 1                | 0                | $\delta_{u_4 s}$ |
| p     | $\delta_{u_1 p}$ | 0                | 1                | $\delta_{u_4 p}$ |
| $u_4$ | 0                | $\delta_{u_4 s}$ | $\delta_{u_4 p}$ | 1                |

The analytic form of the orbitals used was

$$\begin{aligned}
 u_1 &= \left(\frac{2}{\pi}\right)^{3/4} e^{-(r + R_A)^2} \\
 u_4 &= \left(\frac{2}{\pi}\right)^{3/4} e^{-(r - R_A)^2} \\
 s &= \left(\frac{2}{\pi}\right)^{3/4} e^{-r^2} \\
 p &= 2\left(\frac{2}{\pi}\right)^{3/4} z e^{-r^2}
 \end{aligned}
 \tag{6.1}$$

All of the gaussian half-width factors were chosen as unity in order to simplify the numerical work. The values of the overlap integrals were

$$\begin{aligned}
 \delta_{u_1 s} &= 0.043940 \\
 \delta_{u_4 p} &= 0.109850
 \end{aligned}
 \tag{6.2}$$

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The creation of the various states which entered the calculation, their normalization, and the matrix components between them was treated by the spin operator method discussed in the last two Progress Reports. Although this technique makes the problem of non-orthogonality easier to cope with, there is a considerable degree of complexity in the calculation.

Singlet and triplet states corresponding to each type of configuration were set up for both types of interaction and the inversion symmetry of the system was taken account of. The results of the configuration interaction calculation for those states listed in Table 6-1 are given below. \*

| <u>Singlets</u>                      | <u>Triplets</u>                      |
|--------------------------------------|--------------------------------------|
| $H_{ss,ss} = -15.574729$             | $H_{ss,ss} = -15.574655$             |
| $H_{sp,sp} = -12.316543$             | $H_{sp,sp} = -12.273200$             |
| $H_{pp,pp} = -7.866540$              | $H_{pp,pp} = -7.865709$              |
| $H_{ss,sp} = -0.197088$              | $H_{ss,sp} = +0.114860$              |
| $H_{ss,pp} = +0.379815$              | $H_{ss,pp} = +0.379064$              |
| $H_{sp,pp} = +0.160435$              | $H_{sp,pp} = -0.091609$              |
| $(\psi_{ss}, \psi_{sp}) = +0.011763$ | $(\psi_{ss}, \psi_{sp}) = -0.006861$ |
| $(\psi_{ss}, \psi_{pp}) = -0.011883$ | $(\psi_{ss}, \psi_{pp}) = 0.000000$  |
| $(\psi_{sp}, \psi_{pp}) = -0.000047$ | $(\psi_{sp}, \psi_{pp}) = +0.006790$ |

The terms  $(\psi_{ij}, \psi_{kl})$  denote the overlap integrals between the various configurations. The lowest root of the secular equation for the two multiplicities was

$$E(S = 0) = -15.593377$$

$$E(S = 1) = -15.593265$$

The corresponding eigenstates are

$$\psi(S = 0) = 0.998930 \psi_{ss} + 0.003792 \psi_{sp} - 0.048995 \psi_{pp}$$

$$\psi(S = 1) = 0.998549 \psi_{ss} - 0.002158 \psi_{sp} - 0.048979 \psi_{pp}$$

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\*Atomic units are used throughout.

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It is apparent that although the singlet state lies lower than the triplet, the two eigenstates are very nearly degenerate. One can conclude, at least for this model, that the configurations given in Table 6-1 have very little to do with the energy dependence of the spin orientations.

The results for the superexchange configurations listed in Table 6-2 are given below.

| <u>Singlets</u>        | <u>Triplets</u>        |
|------------------------|------------------------|
| $H_{00} = - 15.574729$ | $H_{00} = - 15.574655$ |
| $H_{01} = + 1.181828$  | $H_{01} = - 1.181015$  |
| $H_{11} = - 15.412096$ | $H_{11} = - 15.377591$ |

The overlap integral between the two superexchange configurations was the same for both singlet and triplet cases and was found to be

$$(\psi_0, \psi_1) = - 0.062140$$

The lowest root of the secular equation for each multiplicity was

$$E(S = 0) = - 15.714038$$

$$\Sigma(S = 1) = - 15.703501$$

The corresponding eigenstates were

$$\psi(S = 0) = 0.804649 \psi_0 - 0.545851 \psi_1$$

$$\psi(S = 1) = 0.824139 \psi_0 - 0.517483 \psi_1$$

Clearly the superexchange configurations lead to a description of the system in which the singlet or non-magnetic state lies lower than the triplet or magnetic state. A good treatment of the model can be obtained by leaving out entirely those configurations listed in Table 6-1. It is interesting to note the small amount of energy required to transfer an electron from the central He to one of the end He<sup>+</sup> ions. As a consequence of this the final ground state is almost an equal mixture of the two states  $\psi_0$  and  $\psi_1$  of Table 6-2.

The elements of the secular equation for the singlet and triplet states of the superexchange configurations are nearly identical except for the diagonal energy of the  $\psi_1$  state for the two multiplicities. Apparently the final singlet state is lower lying than

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the final triplet state chiefly because the adjacent unpaired spins appearing in the  $\psi_1$  configuration prefer to set themselves antiparallel rather than parallel. This effect cannot be described solely in terms of sign of the Heisenberg exchange integral.

When the approach of non-orthogonal orbitals is used, one is often tempted to neglect terms involving the square or higher powers of the overlap integral and also three- and four-center integrals. Such an approximation is thought to be reliable in those situations where the overlap integrals are small as is the case for this problem since

$$S_{u_1s} = 0.043940$$

this being the only overlap integral appearing in the superexchange configurations. For the purpose of comparison the results obtained by neglecting these overlap and three-center integral terms are given below.

| <u>Singlets</u>                 | <u>Triplets</u>                 |
|---------------------------------|---------------------------------|
| $H_{00} = - 15.542347$          | $H_{00} = - 15.542347$          |
| $H_{01} = + 1.181454$           | $H_{01} = + 1.201236$           |
| $H_{11} = - 15.445998$          | $H_{11} = - 15.346550$          |
| $(\psi_0, \psi_1) = - 0.062140$ | $(\psi_0, \psi_1) = - 0.062140$ |

The lowest root of the secular equation for the singlet states of the superexchange configurations using this approximation is

$$E(S = 0) = - 15.705045$$

This is to be compared with the energy obtained by carrying the non-orthogonality through properly; this energy being

$$E(S = 0) = - 15.714038$$

The lowest root of the secular equation for the triplet states obtained by the above approximation is

$$E(S = 1) = - 15.690718$$

which is to be compared with the rigorous value of

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$$E(S = 1) = - 15.703501$$

The approximate singlet triplet energy separation is

$$E(S = 0) - E(S = 1) = - 0.014327$$

as compared with the rigorous separation of

$$E(S = 0) - E(S = 1) = - 0.010537$$

We see that even with such a small overlap integral the separation between the final singlet and triplet energies, which is of primary interest here, is given rather differently by the two methods.

There is another interesting piece of information which can be obtained from this calculation. Suppose we were to treat our non-orthogonal orbitals as though they were orthogonal and find the expressions for the various matrix elements of the Hamiltonian on that basis. However, in order to account for the fact that the orbitals are not actually orthogonal, whenever an exchange integral appears in the formulation we set it equal to a Heisenberg exchange integral  $J$ . The lowest singlet and triplet energies will be determined as a function of  $J$  as will the energy difference of these lowest states. For this model there is just one type of exchange integral appearing that being between an orbital located on one of the  $\text{He}^+$  ions and the  $s$  orbital on the central He atom. Again we restrict our considerations to the superexchange configurations. The results for this approach are given below.

| <u>Singlets</u>             | <u>Triplets</u>             |
|-----------------------------|-----------------------------|
| $H_{00} = - 15.639503 - 2J$ | $H_{00} = - 15.639503 - 2J$ |
| $H_{01} = + 0.338732$       | $H_{01} = + 0.338732$       |
| $H_{11} = - 15.390183$      | $H_{11} = - 15.391925 - 2J$ |

If we solve this problem and find the final singlet-triplet energy separation in terms of  $J$ , and substitute the value of the Heisenberg exchange integral, which is

$$\begin{aligned} J_{\text{Heis.}} &= (u_i(x_1) s(x_2) \{ H_1 + H_2 + H_{12} \} s(x_1) u_i(x_2)) \\ &= - 0.024289, \quad i = 1 \text{ or } 4, \end{aligned}$$

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we find the singlet-triplet energy separation to be

$$E(S = 0) - E(S = 1) = - 0.016065$$

This energy difference is to be compared with the value obtained by the proper treatment of the non-orthogonality problem, this value being

$$E(S = 0) - E(S = 1) = - 0.010537$$

We see that even for a problem in which the overlap integral is quite small, which means that our orbitals are nearly orthogonal, an error of approximately 50 percent in the final energy separation is incurred by this kind of a treatment.

Having found the important configurations using non-orthogonal orbitals, the problem can easily be reformulated in terms of orthogonal orbitals. First we set up an s-like function about the central He which is orthogonal to  $u_1$  and  $u_4$

$$s' = s - \delta_{u_1 s}(u_1 + u_4)$$

where  $s$  is the non-orthogonal orbital used above. This gives

$$s = s' + \delta_{u_1 s}(u_1 + u_4).$$

We can now replace the non-orthogonal  $s$  in the states  $\psi_0$  and  $\psi_1$  relating to the superexchange configurations by its expansion in orthogonal orbitals. When this is done and the determinants expanded, it is easily recognized that by using the configurations given in Table 6-4 and carrying out the configuration interaction with these orthogonal orbitals, one would get a final state of energy at least as low as that found by using non-orthogonal orbitals.

Table 6-4

| $u_1$ | $s'$ | $u_4$ |
|-------|------|-------|
| 1     | 2    | 1     |
| 2     | 1    | 1     |
| 1     | 1    | 2     |
| 2     | 0    | 2     |

The same sort of procedure can be used to find the correct set of configurations for the  $Mn^{++}-O=Mn^{++}$  system previously considered. For example, substituting  $d\sigma$  for  $u_1$ ,  $p\sigma$  for  $s'$ , and  $d'\sigma$  for  $u_4$  in Table 6-4 shows the configurations which must

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be included in order to describe the transfer of a  $p\sigma$  electron on the  $O^=$  to the  $d\sigma$  of one of the  $Mn^{++}$  ions in terms of orthogonal orbitals.

Suppose we consider a treatment of the present model by orthogonal orbitals, but in which we leave out the final configuration given in Table 6-4 in which both electrons on the central He have been transferred, one to each  $He^+$  ion. It can be shown that if this extra configuration is not included, it is impossible to get an antiferromagnetic coupling. To do this, we proceed as in the last Progress Report by setting up the Hamiltonian matrix for the singlet states and equating this to the Hamiltonian matrix for the triplet states plus a difference matrix  $D$ .

$$H_{S=0} = H_{S=1} + D \quad (6.3)$$

The form of  $D$  for the superexchange configuration is

$$D = \begin{vmatrix} 0 & 0 \\ 0 & D_{22} \end{vmatrix} \quad (6.4)$$

where  $D_{22}$  is

$$D_{22} = + 2(u_1 s | s u_4) + 2(u_1 s | s u_1) \quad (6.5)$$

Since  $D_{22}$  is positive definite the  $D$  matrix cannot have a negative eigenvalue. If  $\Phi_0$  is the eigenvector corresponding to the lowest lying energy  $E_0$  of  $H_{S=0}$ , then

$$(\Phi_0 | H_{S=0} | \Phi_0) = (\Phi_0 | H_{S=1} | \Phi_0) + (\Phi_0 | D | \Phi_0) \quad (6.6)$$

or

$$E_0 = \mathcal{E}_{01} + D \quad (6.7)$$

But  $\mathcal{E}_{01}$  is surely  $\geq E_1$  the lowest triplet energy, hence

$$E_0 \geq E_1 + D \quad (6.8)$$

Knowing that the matrix  $D$  has no negative eigenvalue shows us that

$$(\Phi_0 | D | \Phi_0) \geq 0 \quad (6.9)$$

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and

$$E_0 \geq E_1 \quad (6.10)$$

Therefore, the lowest singlet energy cannot lie below the lowest triplet energy if one excludes the extra configuration. It is apparent that when using orthogonal orbitals, one must not leave out any configuration that will couple strongly with the low lying states.

Reference

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G. W. Pratt, Jr.



## 7. A SYSTEM OF TWO p ELECTRONS

As was described in the previous Progress Report, <sup>(1)</sup> a system of two p electrons around two atomic cores is treated using Gaussian wave functions and taking into account the configuration interactions. Among all the possible configurations, those treated are shown in Table 7-1. The numbers in the table mean the number of electrons in the corresponding molecular orbital. <sup>(2)</sup>

Table 7-1

| States | $\sigma_g$ | $\sigma_u$ | $\pi_g^+$ | $\pi_u^+$ | $\pi_g^-$ | $\pi_u^-$ |
|--------|------------|------------|-----------|-----------|-----------|-----------|
| 1      | 2          |            |           |           |           |           |
| 2      |            | 2          |           |           |           |           |
| 3      |            |            | 1         |           | 1         |           |
| 4      |            |            |           | 1         |           | 1         |
| 5      | 1          |            | 1         |           |           |           |
| 6      |            | 1          |           | 1         |           |           |

Types of configurations treated were  $^1\sum_g^+$ ,  $^3\sum_g^+$ , and  $^3\Pi_g$ , each of which having contribution from states 1, 2, 3 and 4; 3 and 4; 5 and 6, respectively.

The Hamiltonian has the same form as the one for the hydrogen molecule. The atomic wave function has a form, for instance

$$p_o = 2\sqrt{b}\left(\frac{\pi}{2b}\right)^{-3/4}\left(z + \frac{R}{2}\right) \exp\left[-b\left(\vec{r} + \frac{\vec{R}}{2}\right)^2\right],$$

z-direction being taken along the line joining the two nuclei, and R being the internuclear distance. The only parameter we have is b, which was chosen as unity in the actual numerical computation in order to obtain qualitative information.

The secular equations for  $^3\sum_g^+$  and  $^3\Pi_g$  are quadratic, but those for  $^1\sum_g^+$  states are four by four. It may be of some interest to compare the diagonal elements and the eigenvalues of four by four matrices. These are shown in Fig. 7-1, which looks fairly complicated. Atomic units are used for the internuclear distances and the energies.

In Fig. 7-2, the lowest energy values of the three types of states are shown. From this figure, one can conclude the following: (1) The lowest state is sometimes singlet and sometimes triplet. (2) It is difficult to derive any definite relation between the present model of two p-electron systems and ferromagnetism which might be expected for the crystal composed of p-electron atoms. <sup>(3)</sup>

The author wishes to thank Gloria Freedman for the numerical computation of the four by four secular equations.

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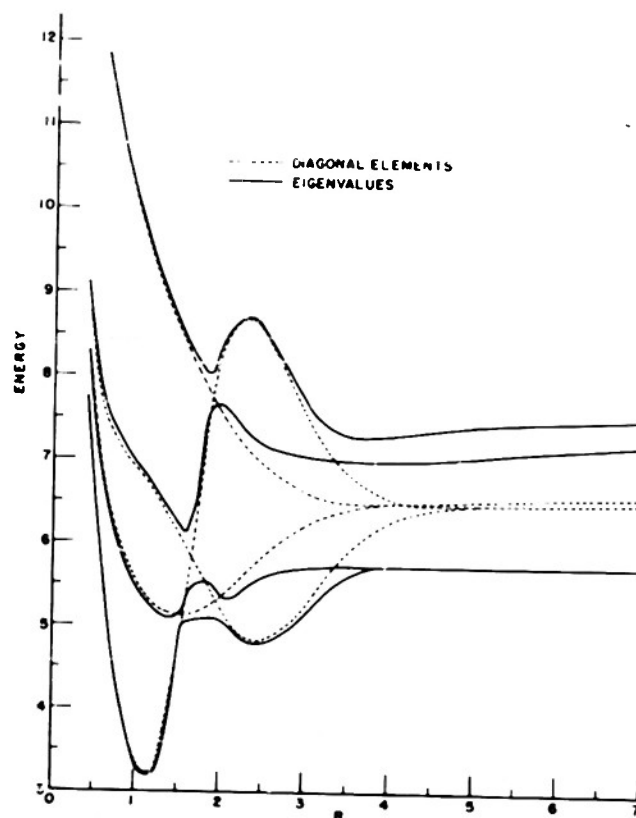


Fig. 7-1

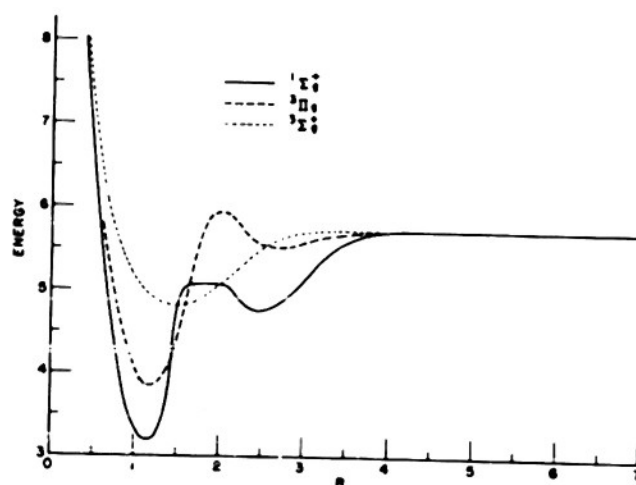


Fig. 7-2

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R. Kikuchi

## 8. CONFIGURATIONAL INTERACTION APPLIED TO THE HYDROGEN MOLECULE

In the molecular orbital treatment of molecules one commonly constructs the orbitals out of orthogonalized linear combinations of atomic orbitals. By choosing a sufficiently large number of these functions, one can get an arbitrarily good representation of the true wave function. This scheme has one unhappy aspect, however. As the difference between the total number of orbitals employed and the number occupied in the isolated atoms is increased, the number of configurations grows at a prodigious rate, leading to secular equations of very great size. One may hope that by employing molecular orbitals constructed more accurately than as linear combinations of atomic orbitals one can get a good representation of the many-electron wave function with only a small number of configurations.

With this hope in mind various molecular orbitals are being used in a study of the hydrogen molecule. One can approximate the true Hamiltonian by the spin free terms, kinetic energy plus electrostatic interactions between the four particles

$$H = -\nabla_1^2 - \nabla_2^2 - \frac{2}{r_{1A}} - \frac{2}{r_{1B}} - \frac{2}{r_{2A}} - \frac{2}{r_{2B}} + \frac{2}{r_{12}} + \frac{2}{R}$$

In this case one may factor out the antisymmetric spin factor and look for a solution of the form

$$\psi_{(1,2)} = \left\{ \sum_i a_i \sigma_i(1) \sigma_i(2) + \sum_{j,k} b_{jk} (\sigma_j(1) \sigma_k(2) + \sigma_k(1) \sigma_j(2)) \right\} \{ \alpha(1) \beta(2) - \beta(1) \alpha(2) \}$$

where the  $\sigma$ 's are one-electron molecular orbitals. Each term in these summations is a singlet, and must be so chosen as to satisfy the symmetry,  $^1\Sigma_g^+$ , of the observed electronic structure.

As the first configuration I chose a function  $\sigma_g^+(1) \sigma_g^+(2)$  constructed from molecular orbitals determined by Coulson<sup>(1)</sup>

$$\sigma_g^+ = N e^{-0.75\lambda} (1 + h\mu^2 + k\lambda)$$

where  $\lambda$  and  $\mu$  are the elliptic coordinates

$$\lambda = \frac{r_A + r_B}{R} \quad \mu = \frac{r_A - r_B}{R}$$

For the internuclear separation  $R = 1.4$  a.u. Coulson found  $h$  and  $k$  by minimizing

\*The 13.54 e.v. atomic units are used here.

(CONFIGURATIONAL INTERACTION APPLIED TO THE HYDROGEN MOLECULE)

$$E(h, k) = \frac{\langle \sigma_g^+(1) \sigma_g^+(2) | H | \sigma_g^+(1) \sigma_g^+(2) \rangle}{\langle \sigma_g^+ | \sigma_g^+ \rangle^2}$$

It seems desirable to add to  $\sigma_g^+(1) \sigma_g^+(2)$  another configuration made of one-electron functions antisymmetric in the nuclei. Coulson's symmetric orbitals are approximate solutions of the self-consistent field equation

$$(-\nabla^2 - \frac{2}{r_A} - \frac{2}{r_B} + \frac{2}{R} + V_{av}) \phi = \epsilon \phi$$

where

$$V_{av}(1) = \int \sigma_g^+(2) \frac{2}{r_{12}} \sigma_g^+(2) d\tau_2$$

As an antisymmetric orbital, an approximation to the lowest antisymmetric solution of this same Schrödinger equation has been constructed in the form

$$\sigma_u^+ = N \mu e^{-\delta\lambda} (1 + c\mu^2 + d\lambda)$$

adjusting  $c$  and  $d$  to minimize the energy. Having thus found  $\sigma_g^+$  and  $\sigma_u^+$ , a configuration interaction was set up between the configurations when both electrons were in  $\sigma_g^+$ , and where both were in  $\sigma_u^+$ . The resulting secular equation, which has been solved, is

$$\begin{vmatrix} \frac{\langle \sigma_g^+(1) \sigma_g^+(2) | H | \sigma_g^+(1) \sigma_g^+(2) \rangle}{\langle \sigma_g^+ | \sigma_g^+ \rangle^2} - \lambda & \frac{\langle \sigma_g^+(1) \sigma_g^+(2) | \frac{2}{r_{12}} | \sigma_u^+(1) \sigma_u^+(2) \rangle}{\langle \sigma_g^+ | \sigma_g^+ \rangle \langle \sigma_u^+ | \sigma_u^+ \rangle} \\ \frac{\langle \sigma_g^+(1) \sigma_g^+(2) | \frac{2}{r_{12}} | \sigma_u^+(1) \sigma_u^+(2) \rangle}{\langle \sigma_g^+ | \sigma_g^+ \rangle \langle \sigma_u^+ | \sigma_u^+ \rangle} & \frac{\langle \sigma_u^+(1) \sigma_u^+(2) | H | \sigma_u^+(1) \sigma_u^+(2) \rangle}{\langle \sigma_u^+ | \sigma_u^+ \rangle^2} - \lambda \end{vmatrix} = 0$$

The integrals involved are all trivial except for the  $\frac{2}{r_{12}}$  integrals, which can be very messy. But as one is able to approximate solutions in the form of exponentials  $n\lambda$  and  $\mu$  times a polynomial in these variables, the Rüdénberg<sup>(2)</sup> scheme may be used directly, and proves very convenient. The papers of Kotani et. al.<sup>(3)</sup> give a partial listing of a set of functions needed in the integration. This table is presently being extended by C. C. J. Roothaan and Klaus Rüdénberg. In the above quadratic secular equation the elements are

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$$\frac{\langle \sigma_g^+(1) \sigma_g^+(2) | H | \sigma_g^+(1) \sigma_g^+(2) \rangle}{\langle \sigma_g^+ | \sigma_g^+ \rangle^2} = -2.26137 \text{ a.u.} \quad \begin{array}{l} \text{Binding Energy} \\ - 3.535 \text{ e.v.} \end{array}$$

$$\frac{\langle \sigma_u^+(1) \sigma_u^+(2) | H | \sigma_u^+(1) \sigma_u^+(2) \rangle}{\langle \sigma_u^+ | \sigma_u^+ \rangle^2} = .16778 \text{ a.u.} \quad 29.48 \text{ e.v.}$$

$$\frac{\langle \sigma_g^+(1) \sigma_g^+(2) | \frac{2}{r_{12}} | \sigma_u^+(1) \sigma_u^+(2) \rangle}{\langle \sigma_g^+ | \sigma_g^+ \rangle \langle \sigma_u^+ | \sigma_u^+ \rangle} = .26528 \text{ a.u.}$$

The binding energy resulting from the configuration interaction is - 3.944 e.v., compared to the Coulson values - 3.535 e.v., an increase of -.409 e.v. by the addition of the second configuration, which is itself energetically very high. The experimentally observed binding energy is - 4.72 e.v.

There are still a number of interesting calculations to be made in this problem. If the energies of the two configurations were closer together, the lower would be pushed down more. Given  $\sigma_g$ , and the form of  $\sigma_u$ , the values of the coefficients in  $\sigma_u$  which minimize the total energy are the best ones to use, and these may not be exactly the same as the values which minimize the energy of the average field equation. I am now trying to solve the secular equation with the  $\sigma_u$  parameters undetermined, to see how well one can do with this configuration, and how far this solution is from the solution of the Hartree equation.

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E. Callen

## 9. THE WATER MOLECULE

Since the last Quarterly Progress Report we have completed all the one-center electrostatic integrals involved in the calculation of the energy for the equilibrium internuclear distance of 1.8 a.u. We have also completed many of the two-center integrals including the exchange integrals involving the hydrogen 1s and the oxygen 1s and 2s wave functions. These expressions involve infinite sums arising from the expansion of the hydrogen wave function about the oxygen center. We have carried six terms in the Legendre function expansion (through  $P_5$ ), with the result that the neglected 1s terms contribute only about  $10^{-6}$  of the total integral, while the error in the 2s sum (after a simple extrapolation) was of the order of  $10^{-4}$ .

G. F. Koster and H. C. Schweinler

## 10. MECHANIZATION OF MOLECULAR ORBITAL DETERMINATION

The Whirlwind program for the self-consistent determination of the optimum linear combinations of atomic orbitals is in the testing and assembling stage. The complete procedure has been broken down into smaller entities, much like the flow chart shown in the last Progress Report, and each part is being made error-free preparatory to combining into one process continuous from the input of integrals to the output of self-consistent eigenvectors and energy levels.

A. Meckler



## 11. LIMITED CONFIGURATION INTERACTION TREATMENT OF THE $\text{NH}_3$ MOLECULE

The greatest portion of the analytic work described in the last Progress Report has been completed. Numerical calculation of all necessary integrals has been started for the observed internuclear separations.

In order to test the accuracy of the numerical integration scheme, which uses a fine mesh to compensate for the relative crudity of Simpson's Rule, the overlap integral between two hydrogen 1s functions on different centers was computed for the internuclear separation of 3 a. u. and the result compared with the exact answer. The results are given below.

|                       |                  |
|-----------------------|------------------|
| Numerical Integration | 0.3485156        |
| Exact Answer          | <u>0.3485095</u> |
| Difference            | 0.0000061        |

Although the hydrogen overlap integral is not the most stringent test of the method of integration, the very accurate result obtained plus the fact that the final energy should be in the first decimal place seem to warrant the conclusion that the accuracy of the final result will not be limited by the scheme of integration.

H. Kaplan

## 12. CONFIGURATION INTERACTION FOR THE FLUORINE MOLECULE<sup>(1)</sup>

By choosing analytic wave functions, it was hoped that the many formulas and tables developed for the purpose could be used to evaluate the two-center atomic integrals necessary for the problem. Kopineck's<sup>(2)</sup> tables, based on the work of Kotani, Amemiya, and Simose,<sup>(3)</sup> are in the most convenient form for use. However, these tables contain only the integrals involving just the 2s and 2p functions on the two atoms. The remainder of the integrals can be computed by means of formulas. Part of this remainder can be expressed in terms of simple expressions, but many can only be expressed in very complicated forms. Because of the limited time that the author had with the Group, it was not possible to complete the necessary calculations. Indeed the time was so short that it did not even seem expedient to start the numerical computation. At the present time the author cannot say anything about the future progress of the problem.

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J. H. Barrett

### 13. NUCLEAR ELECTRIC QUADRUPOLE INTERACTION IN THE KCl MOLECULE

Investigation of the polarized one-electron function:

$$\psi = \psi_{n\ell m}^0 (1 + Cr^\nu \cos \theta)$$

where  $\psi_{n\ell m}^0$  = unperturbed atomic function

C,  $\nu$  = variation parameters

is continuing. A calculation using these one-electron functions in a single determinant representation of  $F^-$  in a uniform electric field is in progress.

L. C. Allen

#### 14. SCATTERING OF NEUTRONS BY $O_2^{16}$

Calculation of the slow neutron differential scattering cross-section for  $O_2^{16}$  is continuing along the lines indicated in a previous Report. <sup>(1)</sup> The cross-section takes account of inelastic transitions between rotational levels of the molecule. Effort is now being concentrated on the evaluation of a number of integrals which arise in connection with the scattering associated with the magnetic spin-spin part of the neutron-electron interaction. It is planned to obtain a total cross-section for comparison with results of experiments under way at Brookhaven National Laboratory.

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W. H. Kleiner

## 15. TRANSITION PROBABILITIES FOR X-RAY EMISSION IN THE TRANSITION METALS

One of the most direct methods used to obtain the characteristics of the energy distribution of the conduction electrons in a metal is through the study of their soft x-ray emission spectra.<sup>(1)</sup> This radiation is caused by the transition of an electron from the continuous band of filled valence levels into an empty inner level of an atom ionized by electron impact. The interaction between the lattice potential and these inner atomic levels is weak, and therefore the corresponding energy levels remain fairly sharp. The continuous band of radiation will therefore be a measure of the distribution of the occupied valence electrons. The correlation cannot however be made directly between the intensity of the emitted radiation and the density of occupied energy states because the observed intensity depends on the transition probability between states. If  $dN/dE$  denotes the number of electrons per unit energy range and  $f(E)$  the probability that an electron in an energy state  $E$  will make a transition to an inner level, the intensity,  $I(E)$ , is given<sup>(1, 2)</sup> as

$$I(E) = f(E) dN/dE \quad (15.1)$$

In the transition metals the valence band is derived from the 4s, 4p, 3d and higher levels, and is pictured in band theory as a wide low-density s-p band capable of holding 2 electrons per atom with a rather narrow d band, capable of holding 10 electrons per atom, overlapping it.<sup>(3)</sup> Because of the higher density of states in the d band the observed emission bands would be expected to represent only the five d bands. Gyorgy<sup>(4)</sup> has recently measured the emission spectra from the transition metals and has found a considerable contribution from the s-like states with a correspondingly lower intensity from the d bands. In order to explain these and other results he is led to assume that the transitions from the s-p band to the 3P level have a greater probability than transitions from the d bands to the same atomic level. The probability of a transition of an electron from a valence state  $\psi$  to an inner level  $\phi$  is proportional to

$$\rho = \left[ \int \phi^* x \psi d\tau \right]^2 + \left[ \int \phi^* y \psi d\tau \right]^2 + \left[ \int \phi^* z \psi d\tau \right]^2 \quad (15.2)$$

and depends on the exact nature of the wave functions involved. Since these wave functions are not known exactly, any calculation must therefore give  $\rho$  only approximately. For the large effect we are seeking, even an order of magnitude calculation seems to be instructive at this time.

For the 3d and more inner levels we choose as our crystal wave functions a spatial Bloch sum of atomic wave functions,  $\phi(\vec{r})$

$$\psi_{\vec{k}}(\vec{r}) = \sum_{\vec{n}} e^{i\vec{k} \cdot \vec{r}_{\vec{n}}} \phi(\vec{r} - \vec{r}_{\vec{n}}) \quad (15.3)$$

(TRANSITION PROBABILITIES FOR X-RAY EMISSION IN THE TRANSITION METALS)

where  $\phi(\vec{r} - \vec{r}_n)$  is the atomic wave function centered at  $\vec{r}_n$ , the vector from the origin of coordinates to the center of the  $n^{\text{th}}$  unit cell. The 4s wave function is chosen as a plane wave orthogonalized<sup>(5)</sup> to the inner Bloch wave functions defined above. The quantity  $\rho$  is then computed from Eq. (15.2) for the case when the initial state is 3d and compared with the value obtained for an initial 4s state. We have fitted the Hartree<sup>(6)</sup> one-electron wave functions for chromium by means of a polynomial times a sum of exponentials in order to obtain analytic expressions for our  $\phi(r)$ . Chromium was chosen because it is the element for which Gyorgy has found the emission bands and for which self-consistent field wave functions are available.

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A. J. Freeman